Rocket Propulsion

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Module No. # 01

Lecture No. # 15

Criterion for Choice of Chemical Propellants

Good morning, today we will start a new topic on chemical propellants.

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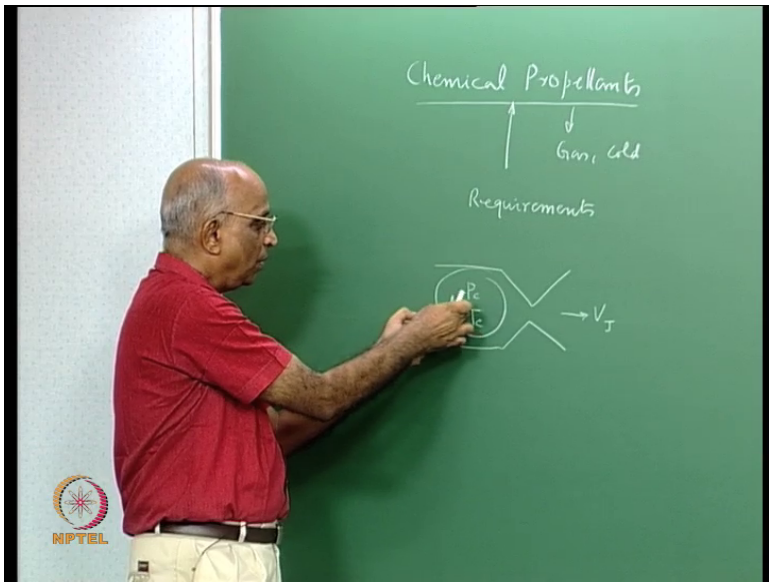

Let us first be clear what we mean by a propellant. We said that any substance used for propulsion of a rocket is known as a propellant. It could be anything, it could be something like a gas, the gas could be cold at high pressure, the gas could be hot. We even considered these boys throwing stones and stones were the propellant. It could be anything; it could be a charged particle, it could be a plasma. But what we consider in the next three classes is chemical propellants.

This brings us to chemical rockets, which use chemical propellants. The chemical rockets are solid propellant rockets, liquid propellant rockets, hybrid rockets and so on. Therefore, let us see what are the requirements of propellants in these rockets since

before we study the propellants; we must know what are the requirements. What is the requirement of a propellant? I think that is the basic with which we should get started.

We studied that nozzles were an integral part of a rocket; let us say that this is a chamber and you have a nozzle which is connected to it and the aim is to get as high as a jet velocity as possible. And to get a high jet velocity we found that we required a high value of the chamber pressure and a high value of the chamber temperature.

We also found that we require a small molecular mass of the gasses, which are being expanded out. In this case I will get a higher jet velocity and what was the term that we used? We used the term C* which is a transfer function between what is sent into the combustion chamber and the high pressure, high temperature, low molecular mass combustion gases which are generated. And what was the expression for C*? We had the expression, $C^* = \sqrt{RTc}/\ \Gamma$. Here R is the specific gas constant which in terms of the universal gas constant R_0, we could write it as R_0/M where M is the molecular mass of the gases which are sent out through the nozzle. Tc is the temperature of the hot gases. And Γ is a function of γ. Therefore, this expression for C* should tell us what we really require of a propellant in a rocket.

What we require is that this transfer function which tells the capacity of this particular chamber to generate high pressure gases must be high or rather this characteristic velocity C* must be a large number. The transfer function C star of the propellant of the chemical propellant must be large.

If C star has to be large obviously Tc must be large. The molecular mass of the gas escaping through the nozzle must be small. Anything else? We have the combination of γ in Γ: we found that gamma must be small because $\Gamma = \sqrt{\gamma}(2/\gamma+1)^{(\gamma+1)/2(\gamma-1)}$. The requirement was that gamma should be small.

Γ, however, is not as sensitive and influential as Tc and molecular mass of the gas. Therefore, basically we are looking at the following parameters: Tc to be large and the molecular mass of the gases to be small; may be the specific heat ratio also to be a small number. If I can have propellants which could generate gases such that the temperature of the hot gases and the pressure of the gases could be large. The molecular mass of the gases should be small and the specific heat ratio of the gases must be small. This is what a propellant be capable of.

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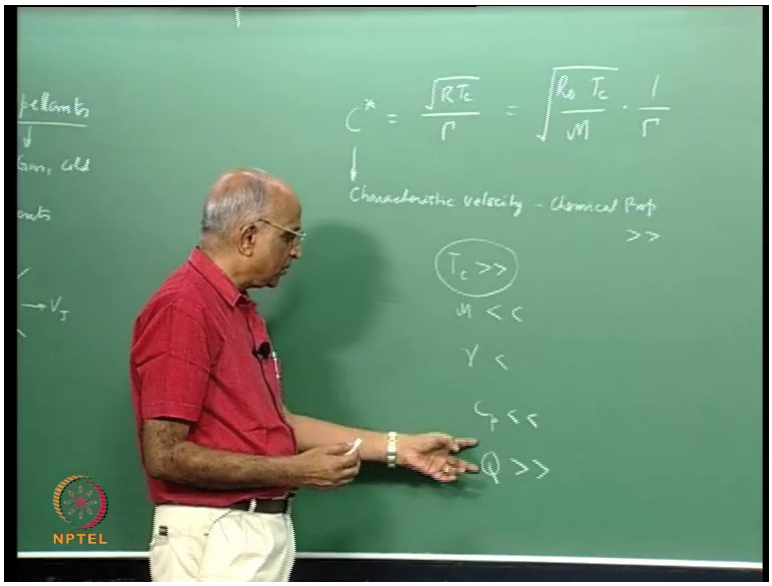

Let us first take a look at temperature Tc: What will give me a high value of Tc? If we have a chemical propellant and now we must say we are talking of chemicals, there are a large number of chemicals available. And why do we use chemical substances? May be I want the chemicals to react with each other and generate hot gases. Why hot gases? If I have hot gases we have a temperature Tc, which could be a high. Therefore, basically we are looking at chemicals, which could react and generate hot gases and these hot gases could be at a high temperature. To generate a high temperature gases the heat released in the chemical reactions should be large.

We consider unit mass of propellant and denote heat generated by unit mas of propellant in the chemical reaction. The heat release per unit mass is required to be large. If the heat release is divided by the mean value of the specific heat of the gases, say at constant pressure, we get the temperature increase from the chemical reactions of the propellants. If the specific heat at constant pressure is small, we can have a larger value of temperature Tc for the same heat release.

We have now introduced one more term viz., specific heat of the gases as a requirement. What we are saying is if we have chemicals these chemicals react generate to hot gases at high temperature. When do we get high temperature? If the heat release per unit mass of the chemical propellant is a large number and if the specific heat Cp of the burnt gas is small.

Therefore, we now state that the specific heat of the gas generated by the chemical reactions must be also small.

These are the requirements that we are looking for are that the chemicals should have a large value of heat release, a small value of specific heat and a small molecular mass of the product gases that are generated at high temperature and also perhaps a small value of γ.

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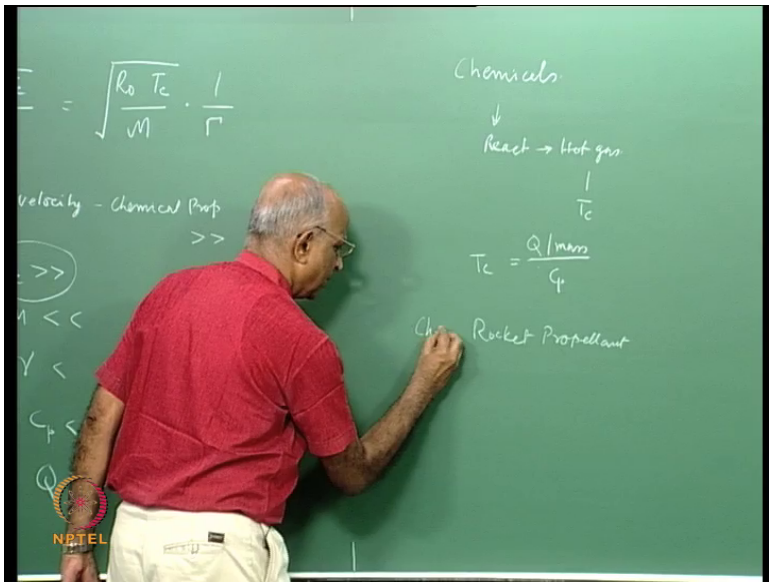

If we can address all the above parameters together, maybe we can narrow down a few chemicals out of the millions chemicals that are available which can be used as chemical rocket propellants or as rocket propellants. Which of the chemicals are suited to be rocket propellant? And this is what we are going to address in this class. Therefore, let us ask how we will get high values of heat release, small value of molecular mass of the gas and low specific heat of the reacted gas? Let us start with something simple; under what conditions will we get low molecular mass of the gases that are generated in the chemical reaction?

Let us say we have a chemical substance and the reaction of the substance generates hot gas. Therefore, basically we must take a look at the atomic mass or the mass of the elements in the chemical substance. If the elements are of small atomic mass, the product gases formed by chemical reaction would also be small.

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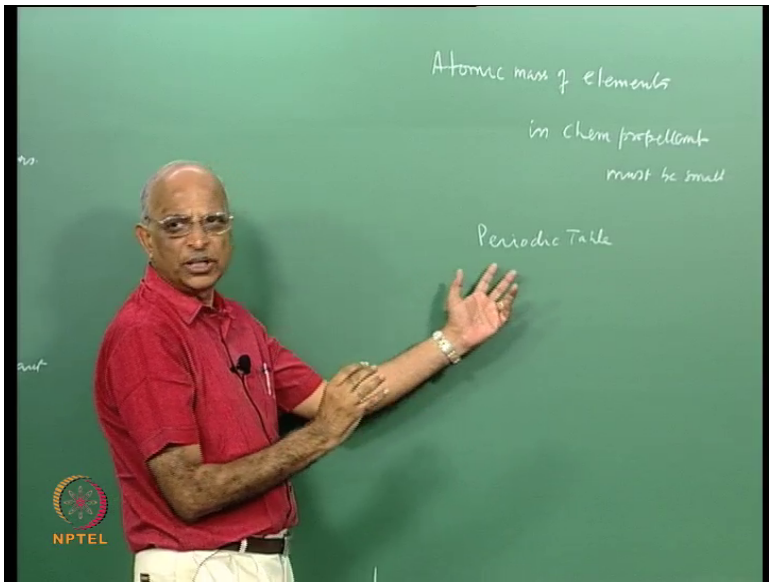

If the atomic mass of the elements in the propellant is small the product gases will also have low atomic mass. First let us take a look at the periodic table. What is there in a periodic table? All elements are arranged in terms of their atomic number and this is what we will first take a look at it. Let us take a look at the periodic table starting with elements having an atomic number of 1. The atomic mass of hydrogen is unity and its atomic number is 1. The next is helium the atomic number is 2 and its atomic mass is 4. Next is lithium. The atomic number is 3 and the mass of lithium atom is 6.9. Beryllium 4 atomic mass is 9. Boron 5 the atomic mass is 10 and so on carbon 6, atomic mass 12 and so on.

Next then to oxygen, nitrogen, fluorine we have neon an inert gas, then we have sodium, magnesium, aluminum, silicon, phosphorous, sulphur and chlorine. We stop at atomic number of 17 because already the atomic number has increased to 17 and as you see the atomic mass has increased from 1 to almost 36. The values of the atomic mass are given are with respect to hydrogen. Beyond this the atomic mass of elements becomes large such that that any product which is formed will have larger values of the molecular mass i.e., become very heavy. What does this Table tell us? Let us take a particular case may be hydrogen with the lowest atomic mass. Even if I take a hydrogen molecule H_2, the molecular mass is 2.

The molecular mass is lower than other molecules or substances. Therefore, it is a very viable substance that could be used as a propellant from the molecular mass point of view. We next go to helium. Helium is inert. It can be used as an inert gas but cannot be used as a chemical propellant. Next, lithium is used in solid propellants because of its low atomic mass. We will have to take a look at it when we study solid propellants. Beryllium and boron can be used; the masses are still small with atomic mass of 9 and 10. Carbon is a part of any hydrocarbon; carbon and hydrogen together. Well we cannot escape from hydrocarbon and is suited as the atomic mass is not too large. Fortunately for us carbon has an atomic mass of 12, which is still not very bad. Next in the periodic table is nitrogen; it is inert, but most of the substances in nature are associated with nitrogen. The atomic mass of nitrogen is 14.

Oxygen is a powerful oxidizer. It has an atomic number of 8 and an atomic mass as 16. The molecular mass of oxygen O_2 is 32. Fluorine is a very reactive oxidizer, much more reactive then oxygen and its molecular mass is very near to oxygen itself; its atomic mass is 19. Neon is inert I cannot consider it for chemical reactions. Sodium is a very reactive metal. If we drop sodium in water it just explodes and to use it would be impossible. Magnesium: you would have seen magnesium ribbon being used as a diwali cracker, you could light it and it burns as a reactive metal. It is quite reactive therefore, it may be difficult to use magnesium as it is.

Aluminum is a light metal of atomic mass 27. If we have to use a metal in a propellant, it appears better to suggest aluminium. Other metals would be very much heavier. Only aluminum is used. Iron is seldom used. Silicon is a light material, but it is not reactive. We will not consider phosphorous as it is very reactive. We cannot consider sulphur and chlorine since these also have high atomic mass of 32 and 35.5 respectively.

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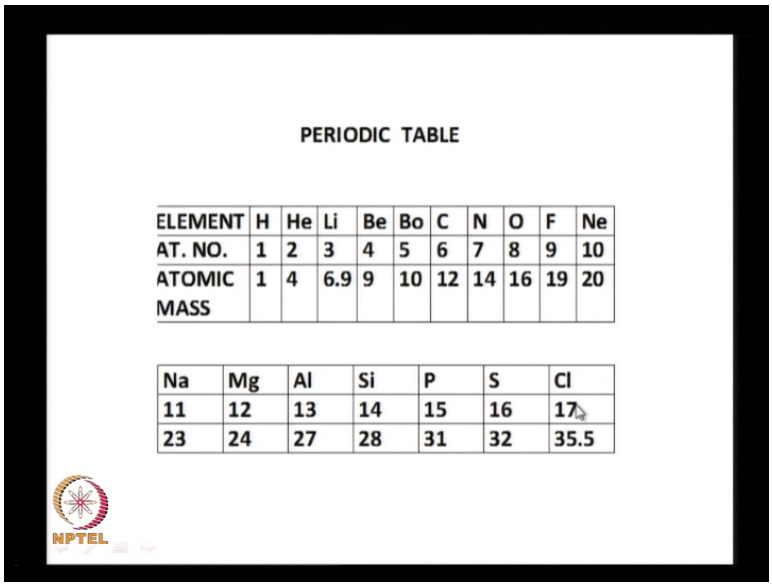

Beyond this you know you go to argon and other elements and they becomes progressively more and more heavier and they cannot be used. Therefore, all what we say is out of all the chemicals that we can think of using, we can now isolate those containing elements upto chlorine which has an atomic number of 17.

From the molecular mass point of view, therefore, we prefer the lighter elements. I show these elements again in the next slide where in we see the relatively lighter elements hydrogen, lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, aluminum, sulphur and chlorine.

Well these elements, if contained in the chemicals, would be better since low value of molecular mass in the reacted products is more desirable. Therefore, we address the first point of choice of the substances from the molecular mass point of view. When will the molecular mass of my products be small? When the atomic mass of the elements that constitute it are small.

Fluorine is very reactive; it is more reactive than oxygen. In fact it was tried for rockets but it was very reactive and would corrode even the propellant tanks. It was used in one of the Delta rockets; however, it has not been subsequently used. We will keep it in mind and see under what conditions fluorine can be used.

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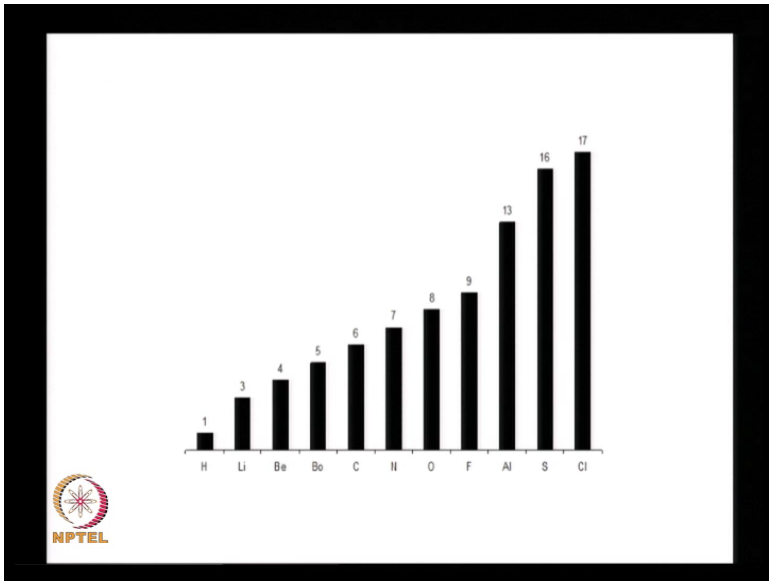

Oxygen, fluorine, chlorine are oxidizers. Hydrogen, carbon, lithium, beryllium, boron, and aluminum are fuels. Aluminum is a metal, which can burn and release heat. All of you would have observed a sparkler during Diwali festival. The sparkler consists of a composition which is known as a black powder composition and it is coated on a on a rod may be a steel rod or something like it.

In some instances metal powder or filings are added to the composition in the sparkler. When the sparkler with the metal filings or metal powder burns, it burns much more violently. This is because the burning or combustion of the metal releases much more energy. Therefore, metals such as aluminum, boron, beryllium can also be used very effectively as fuel. Therefore, we now conclude by stating that low atomic mass elements are more desirable in a propellant from molecular mass point of view of the products.

Let us now take a look from the temperature point of view on whether we should have some of these elements or what should be the composition of the chemicals in the propellant such that we get a high value of temperature.

May be if we go through this aspect, about half of our work in choosing a propellant will be over. For high temperature, we needed high heat release and low values of specific

heats. Let me come to the second part on specific heats before looking at heat release from chemical reactions in a propellant.

We had said that the products of burning or of chemical reaction in the combustion chamber of a rocket are released through the nozzle. The temperature of the hot gases Tc goes as heat released divided by the specific heat and therefore we would like to have Cp as small as possible. Single atom like oxygen atom, hydrogen atom i.e., mono atomic species have a specific heat of the order of something like 20 joule per mole Kelvin. Unit of specific heat is per mole per Kelvin. If we have di atomic molecule like O_2, hydrogen H_2 or OH that is two atoms of the elements, the specific heat increases to something like 35 joule per mole Kelvin. If we still have more complicated molecule like CO_2, 3 of atoms together, the specific heat increases to almost like 62 or 63.

Let us say that the specific heat of the triatomic molecule is 65 joule per mole Kelvin. Why should specific heat increase as the molecule changes from mono atomic to di atomic to tri atomic? What will be your reaction? Why should it increase? Mind you the unit is per mole Kelvin.

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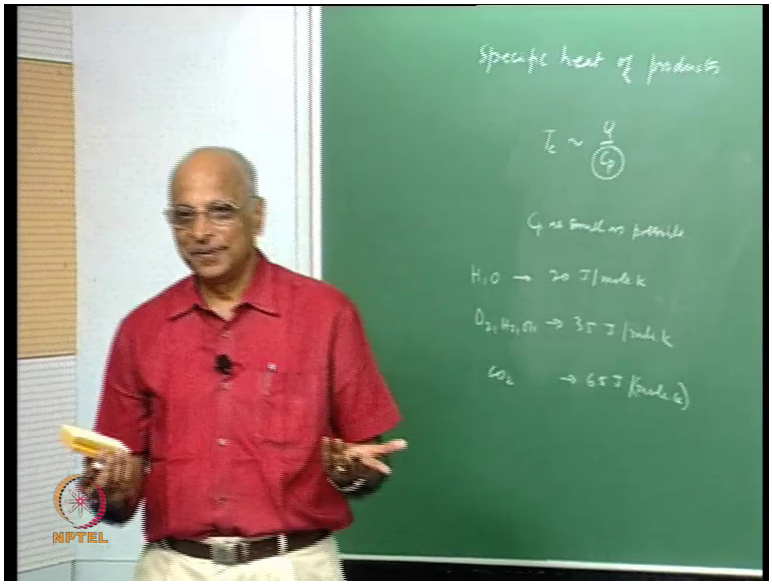

Why should the specific heat go up? If we take a simple atom, let us say like oxygen atom it is just O, if I take a molecule O_2: 2 well it has two O atoms. We are not bothered about double bond single bond and how the two O atoms are bonded together. When we heat say the O atom, it has smaller degrees of freedom and it therefore absorbs less

amount of energy. This will absorb more energy if it could have more degrees of freedom. A relatively more complex molecule like CO or CO_2 has more bonds and more degrees of freedom. It can absorb more energy. Therefore, the energy absorbed per mole of a mono atomic substance is less, di atomic is more, tri atomic is still higher and so on it increases.

Therefore, let us see the variation of the specific heats. A mono atomic substance has the lowest, di atomic has higher value, tri atomic has still has a higher value and as we go on the value of the specific heat keeps increasing. Therefore, from this point of view we should say if the product gases are all mono atomic, we are better off. A di atomic gas is to be preferred to a mono atomic gas. What this implies is that the product of combustion or reaction of the propellants must be simple not complex, in which case I can have a smaller value of the specific heat in Joules per mole per Kelvin.

I show some of the values of Cp in the next slide. Helium is mono atomic. At the two temperatures of 2000 Kelvin and 3000 Kelvin there is hardly any change in specific heat. Therefore, irrespective of temperature for the mono atomic may be helium, hydrogen atom, oxygen atom the value is around 20 Joule per mole Kelvin. If we go to di atomic gases; hydrogen H_2, hydroxyl OH or may be HCl or may be N_2 or CO, all have a ball park number of around 35 Joules per mole kelvin. A change in temperature does not markedly change the value of specific heat.

When we have tri atomic gases, the values of specific heats are even higher; well of the order of 60 to 65 Joules per mole Kelvin - something like 60. Water is around 51 to 58 Joule per mole Kelvin, CO_2 is between 60 and 63 may be around 63 to 64. We find that mono atomic substances have specific heats around 20 Joule per mole Kelvin, diatomic around 35 to 36 while triatomic substances have specific heats around 60 to 65 Joule per mole Kelvin. Therefore, this is the range and based on this it is preferable for the product gases to be more dissociated if we want high temperatures.

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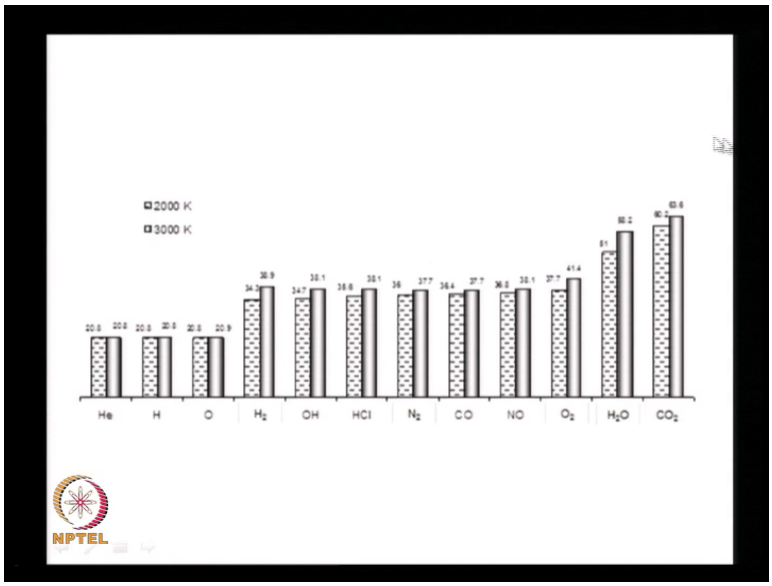

If we keep on increasing the value of specific heats, we will not be able to get a high temperature and therefore, we said that the specific heat of the product gases must be small. We have looked at two criteria namely we looked at the criterion of molecular mass and find that the atomic mass must be small or atomic number must be low. Second we found that from the specific heat point of view of the product gases (which result from the chemical reactions of the chemicals) must be somewhat simple or disssociated. Let us go to the next criterion before we come back to the temperature and heat release. Let us take a look at γ, the ratio of specific heats. We had said that γ should also be small in order to get a high value of jet velocity V_J.

What does this small value of γ imply? If we go through thermodynamics and the kinetic theory of gases, we find that γ is defined as Cp/Cv, which in terms of the degree of freedom (n) of the molecule can be written as $1 + 2/(n+3)$. The value of n shows the degrees of freedom of the gas over and above the translational modes. Let us illustrate this. If we have an oxygen atom; it can either move in the three directions, along X, Y and Z. This means it has 3 degrees of freedom along the three translational axes. If we have an oxygen molecule well it has it has in addition to translation in the 3 directions rotational motion also. The oxygen atoms in it could also vibrate.

Therefore, it has additional degree of freedom of 2, compared to the atom, which only translates. I could also have atoms in which we have may be C_3H_8, which becomes more

complicated it could have many more degrees of freedom compared to simple translation. And for instance if I take CCl_4, carbon tetrachloride, the degrees of freedom are almost something like 13 or 14. As the molecule becomes more complex, it has more degrees of freedom.

Therefore, the value of gamma value for a mono atomic gas, for which the number of degrees of freedom is 3 is determined by the following: the value n gives the degrees of freedom. We say for mono atomic gases like let us say γ for helium is equal to 1+2/3, which is equal to 1.67.

For di atomic gases like oxygen, hydrogen, nitrogen molecules we have two additional degrees of freedom from rotation and vibration. The value of γ is 1+2/5, which is 1.4. May be as it becomes very complex like γ for CCl_4, carbon tetrachloride, is going to be something like 1+2/(13+3) or so giving γ about 1.13. That means that more complex the molecule, it has a lower value of gamma. If therefore γ is required to be small, then the gases, which are passing through the nozzle should have should be more complex.

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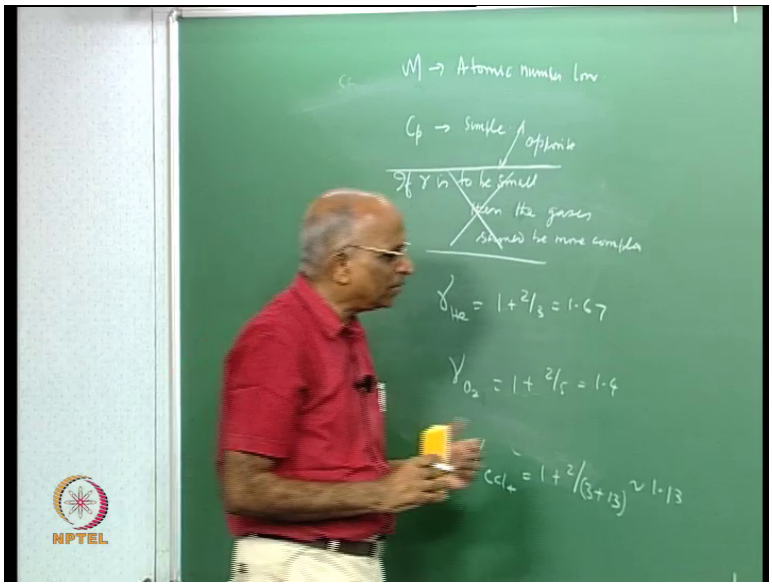

The requirement for γ to be small calls for the gases to be more complex, but for Cp to be small the gases must be simple. These two criteria call for just the opposite requirement. Similarly, if you want the atomic mass to be small; we are also thinking of simple product gases therefore, we find that gamma requirement is somewhat contrary to the requirements of Cp and also molecular mass in the product gases. Therefore there is a

problem and we also know based on what we have studied so far from the nozzle theory that V_J is not very sensitive to gamma. Therefore, we will not give very much importance to gamma as for specific heat and molecular mass.

To summarize, the Cp of the product gases should be small which necessitates that the product gases must be in a dissociated form as simple molecules. The molecular mass of the gases would then also be small. However, then a small value of gamma cannot be obtained as the value of gamma decreases as the complexity of the gas increases. We give less weight age to gamma because Cp directly impacts into temperature and C star is inversely proportional to the molecular mass.

We are left with heat release to be able to determine the value of temperature Tc. Let us take a look at heat release in a chemical reaction.

Let us have a chemical substance and we call it as C_1. This chemical gets converted to gas like a product let us say P_1. We are looking in this case of this chemical by itself reacting to give P_1 or else we have substances C_1 plus C_2 reacts to give us P_1, product 1, P_2, product 2… The question is how do we determine the heat released in these reactions? These are all chemical reactions of substances giving the products or chemical reaction between two chemicals, which give us products. And we are interested in determining the energy from the chemical reaction.

We have studied about this both in the combustion course and in the course on explosion physics. We had said that any substance would have its own internal energy? We called it as chemical internal energy of the substance. Now, if it gets converted to products and it will also have some energy like chemical internal energy of the products. In a chemical reaction, the reactants get converted to products. If you have more energy of the reacting chemicals compared to the products, the deficit of energy is what is obtained as heat of a reaction.

Let us elaborate. Suppose we have some chemicals; these chemicals have some energy. As an example, this duster has some energy. Where does the energy come? I have all these bonds together in the wood; it has some energy. Now I burn it and I get carbon di oxide, carbon mono oxide or whatsoever it may be. If the energy which is available before the burning (i.e., the reaction) is more than the energy of the final products, which

are formed in the reaction, then since the energy cannot get destroyed, the deficit or reduction manifests itself as heat and that is the heat of a reaction.

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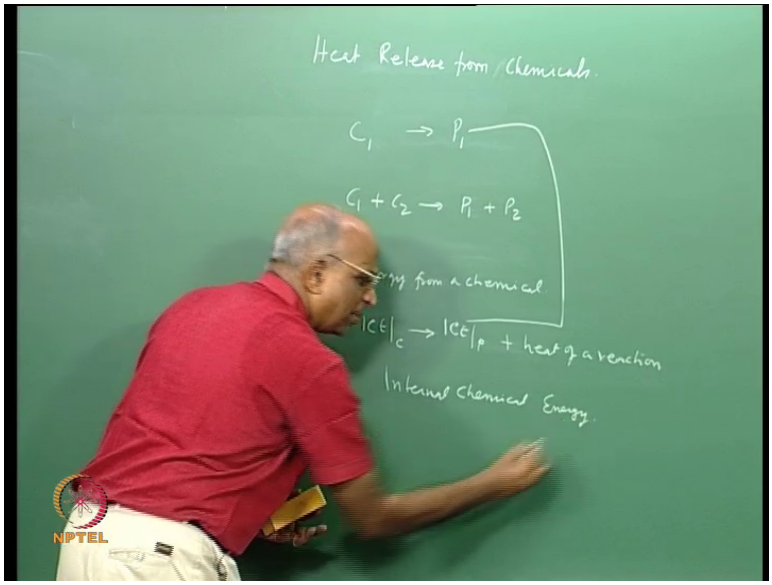

Therefore, basically we need to find out what this internal chemical energy or what is the chemical energy available in the chemical, which we call as internal chemical energy. You know the word given to describe this internal chemical energy is heat of formation. And how to define the heat of formation? The heat required to form a substance - any substance - at standard state from its elements again at standard state.

We need to be able to describe what is the energy available in a given chemical and to be able to do so we need certain standard conditions.

Well. At the standard condition what is the energy available in the chemical substance. This substance could be let us say hydrogen, carbon, nitrogen or some arbitrary substance like $H_aC_bN_c$. What are the elements, which constitute this arbitrary substance? They are again hydrogen, carbon as a solid, nitrogen combined in a certain way and mind you these come from elements or elemental substances. Hydrogen is a gas under standard conditions, carbon is a solid under standard conditions, nitrogen is a gas under normal conditions.

And the standard condition is taken as 25^oC and one atmosphere pressure. In other words if we want to form a substance at the standard condition from its elements again at the

same standard condition, the energy required to form the substance is known as heat of formation. The notation for the heat of formation is as follows: we have to give some heat, which is enthalpy to form H_f. We have to give enthalpy, some increment Δ in enthalpy to form the substance from its elements. We form it at the standard condition from its elements at the same standard condition. Superscript '0' shows the standard condition. Therefore, ΔH_f^0 denotes the heat at standard condition of the substance and the elements from which it is formed and subscript of "f" is the notation for heat formation of a substance.

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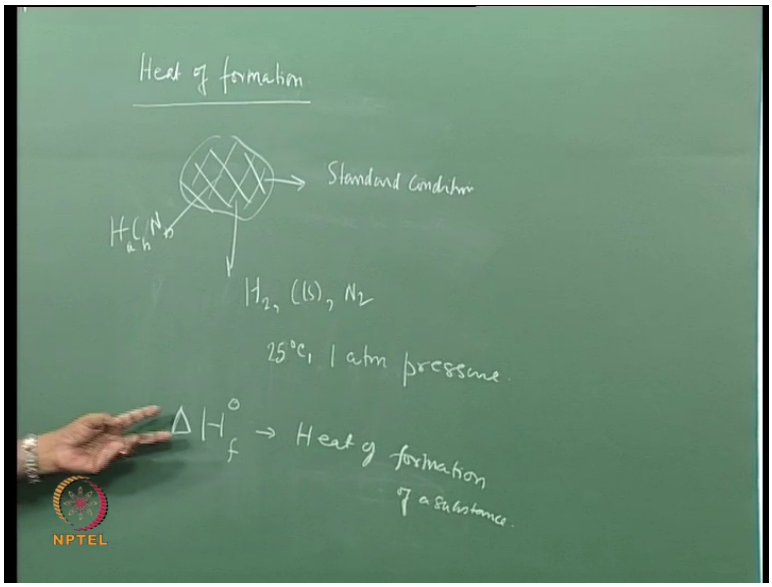

If we know the heat of formation of a substance, then we have its internal chemical energy. If a substance C_1, which is a chemical substance has a certain heat of formation and if the product formed has a given heat of formation, the decrease or the reduction in the heat of formation from reactant to product gives the energy released in the reaction. The decrease, in the heat of formation, shows that heat is generated in the reaction. The reaction, we say, is exothermic; we get some heat from the chemical reaction. This is how we go about finding out of the heat generated in a reaction.

Let us assume that I have a fuel F, I have an oxidizer O and their combination causes a chemical reaction, which produces the products. Fuel could be any fuel may be I take wood as a fuel or oxygen as oxidizer or use the air as an oxidizer and I get some products it like CO_2 or may be CO.

Therefore, now we say that the chemical reaction between fuel plus oxygen gives us say CO_2 plus CO. If the fuel contains hydrogen also may react with oxygen to form H_2O as products. Let us say the reaction takes place between a_1 moles of the fuel with a_2 moles of the oxidizer to give b_1 moles of the first product (say CO_2), b_2 moles of second product (say CO) and b_3 of the third product (say H_2O). Therefore, what is the energy released in this particular reaction? We have to consider the moles of the substances and suitably define the heat of formation in terms of joules per mole. If the net heat of formation of the products is less than the net heat of formation of the reactants, heat is generated in the reaction. Let us therefore look at heat of formation of a substance.

The heat of formation of a substance ΔH_f^0 is the heat required to form 1 mole of the substance at standard condition from its elements again at the same standard conditions. Heat of formation has units of joule per mole. And this is the mole; a_1, a_2, b_1, b_2, b_3. The heat of formation of the products is b_1 moles into heat of formation for CO_2, plus b_2 moles into heat of formation of CO plus b_3 moles into heat of formation of H_2O. This is the value of the total heat of formation of the products over here. What is the heat of formation of the reactants? It is equal to a_1 moles into heat of formation of fuel F plus a_2 moles of oxidizer O into heat of formation of the oxidizer.

We have standard sign “0” to indicate the standard conditions. Since heat energy is released when there is a net decrease in the heat of formation, we denote the heat energy released in the reaction with a minus of the decrease. The heat energy is equal to minus of heat of formation of the products minus the heat of formation of the reactants.

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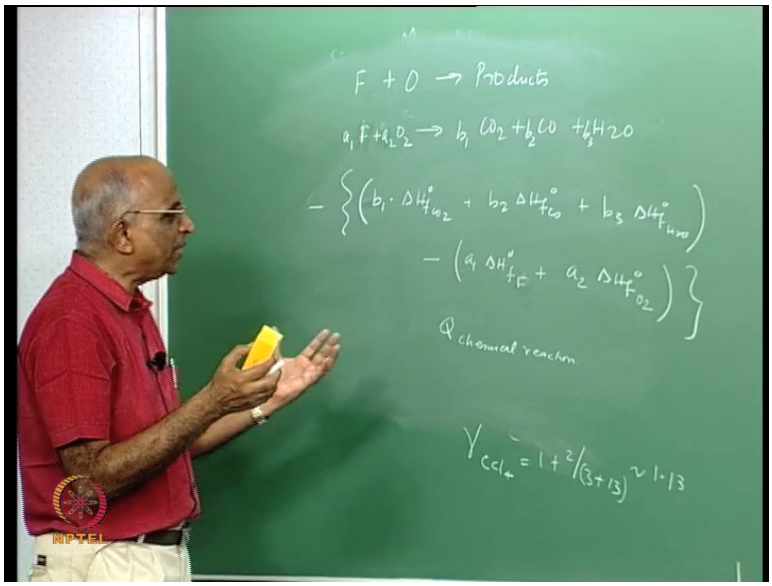

We would like to know which are the chemicals, which can release lot of heat energy thereby making a good choice of the chemicals to be used for the propellants. Could they be characterized in terms of their heats of formation at the standard conditions? Let us therefore take a few examples. Let us form carbon dioxide from carbon. We do an experiment. We take carbon at the standard state. And carbon at the standard state of 1 atmosphere pressure at temperature of 25°C is a solid.

We react it with oxygen, which is a gas and the oxygen is again at 25°C and one atmosphere pressure and I from carbon dioxide. Again we form it at 25°C and at one atmosphere pressure. The energy required to form carbon dioxide gas from its elements C in solid viz., C(s) and O_2 as gas will give us the heat of formation. But all of us know, if we take carbon and burn, it gives out some amount of energy, which is quite significant amount of energy. And the energy which we get from burning 1 kilogram of carbon is something like is 32,800 kilo joules; kilo joules per kilogram of carbon burnt.

That means when we burn element carbon with element oxygen, then per kilogram of carbon burnt, we get something like 32,800 kilo joules of energy. Now, what is going to happen? This 32,800 kilo joules of energy is not going to form carbon di oxide at 25 degrees; rather the temp of carbon di oxide will go up. If the product carbon dioxide has to be at 25 degrees centigrade, what is it we have to do? We have to remove this heat

from this reaction. This means I have to remove i.e., minus 32,800 kilo joule per kg of carbon burnt so, that the product CO_2 can be at 25^oC.

Carbon and Oxygen are elements at the standard state. Since the heats of formation are defined with reference to the elements, the standard heats of formation of the elements at the standard condition would be zero. Therefore, the standard heat of formation of CO_2 should be – 32,800 kilo joules per kg of carbon burnt. But there is something wrong with the units here. We defined standard heat of formation as the heat required to form one mole of the substance from its elements when both the substance and the elements are at the standard conditions. We cannot state it in terms of kilogram of carbon but rather must be expressed in terms of one mole of carbon di oxide. Let us try to remedy the situation. For expressing in terms of one mole of carbon di oxide, we note that for every mole of carbon burnt, one mole of carbon di oxide is formed. This implies that for every 12 g of (0.012 kg) carbon, 1 mole of CO_2 is formed. The energy, which is released is equal to 1 mole of carbon di oxide is therefore equal to $32800 \times 0.012 = 397$ kilo joules per mole.

What is it that we had to do while forming carbon di oxide at the standard conditions? We had to remove the heat and that the heat of formation at standard state of carbon di oxide is therefore equal to −397 kilo joules / mole of carbon dioxide.

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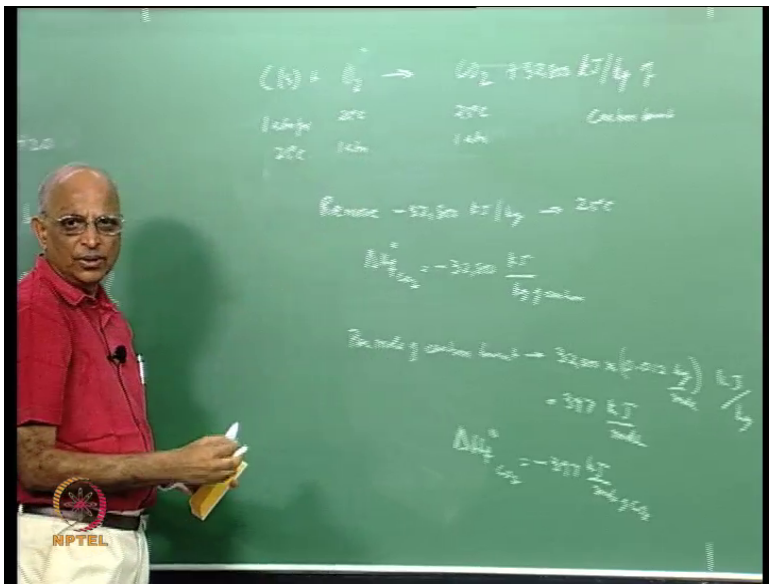

By now you would have guessed that for any reaction which is exothermic, the net heat of formation of the products will be less than the net heat of formation of the reactants.

Large negative values of the standard heats of formation of the products will be favorable for more heat release in a reaction. Let us take one or two small examples because this is something, which is basic. Let us take the reaction of 1 mole of carbon as a solid at element level reacting with half mole of oxygen both at standard state forming 1 mole of carbon mono oxide. Now, I have carbon mono oxide here instead of carbon di oxide. It is not fully oxidized. The heat, which is generated in the reaction, if we do an experiment is something like 9208 kilo joules per kilogram of carbon burnt.

Therefore, we quickly convert it for per mole of CO formed. In order to form one mole CO, we need to burn 0.012 kilogram of carbon to get 9208×0.012 - so much kilo joules per mole of CO. This is because one mole of carbon monoxide is formed from one mole of carbon. And this is equal to 110.5 kilo joule/mole. Since heat is getting generated as CO is formed, we have to bring it back to the same standard condition of $25^{o}C$ degrees of oxygen element and $25^{o}C$ of carbon element. The heat of formation of CO is therefore −110.5 kilo joule/mole.

Hydrogen and oxygen react to form water. The reaction is given by 1 mole of hydrogen reacts with half mole of oxygen giving 1 mole of water (H_2O). Why do we take this example? Hydrogen is an element gas at $25^{o}C$, oxygen is an element, a gas at $25^{o}C$, but water should be a liquid at $25^{o}C$. We can say that the heat of formation water as a liquid at standard condition should be equal to the negative of the heat release in this reaction, which is 286 kilo joule/mole of water.

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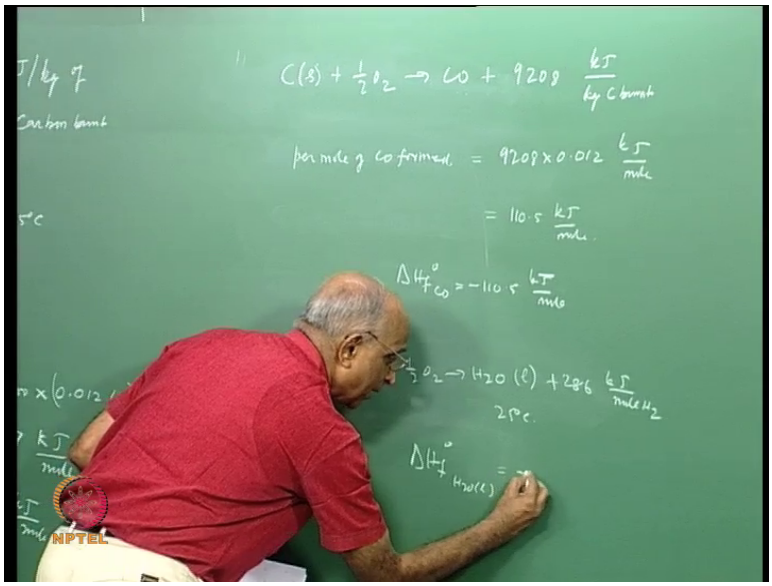

Now we are expressing heat of formation in terms of per mole; heat of formation of H_2O as a liquid (water) is equal to −286 kilo joule/mole. 1 mole of hydrogen forms 1 mole of water and this is how we determine the heat of formation. Please let us not forget that the heat of formation of a substance is defined with respect to the elements that constitute it. The heats of formation of the elements themselves are therefore 0 at the standard state. One last substance I should consider with a positive heat of formation. Let us take the formation of hydrogen as an atom. We could consider 1 mole of H_2 dissociating to give 2 moles of H atom.

What we do in this case? We need to supply heat to be able to form hydrogen atom from the hydrogen molecule, which occurs naturally. The amount of heat required to dissociate 1 mole of hydrogen is about − 435 kilo joules per mole of hydrogen. And the reaction is endothermic. Therefore, heat of formation of H is equal to + 435 for 2 moles of hydrogen. For each mole of hydrogen atom, the heat of formation is therefore + 217.5 kilo joules/mole. And this is plus because the formation of hydrogen atom from the elements is endothermic I have to supply heat to form hydrogen atom from the naturally occurring element hydrogen and it is + 217.5 kilo joules/mole.

Therefore this is how the standard heats of formation of different substances are determined. However, we need not do an experiment to determine the heat of formation of a substance. If we have, let us say a hydrocarbon. The bonds between carbon and

hydrogen and between the carbon atoms are known. We know the energy of each of the bonds then we know the energy of the bonds of the basic elements. We subtract the bond energy of the product or the substance from that of the element and we get the value of the heat of formation. But there are certain problems, which come while estimating heat of formation from bond energies. A substance does not only have energy of the bonds, it could have energy in some resonance modes.

It is necessary to have bond energy plus resonance energy of the substance minus the bond energy of the elements, which will give us this is the way of theoretically calculating the heats of formation. Details of estimation of heats of formation from bond energies are given in the textbook on "Chemical Problems in Jet Propulsion" by Penner.

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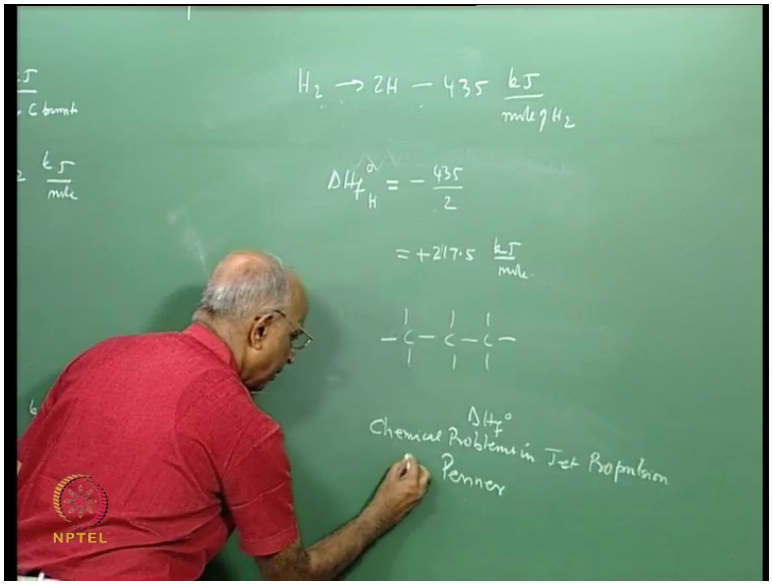

He gives a good treatment of heat of formation in the book. With the understanding that we have developed for heats of formation, let us see if we can make some recommendations for the choice of propellants.

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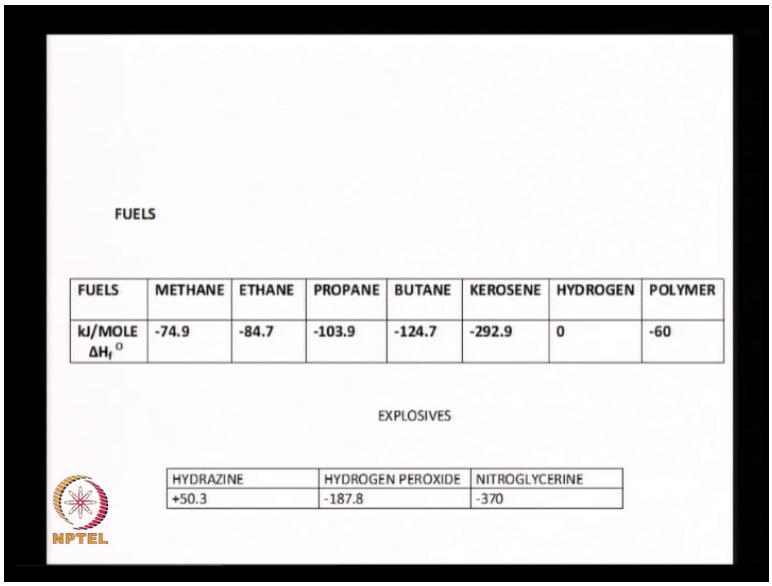

I will quickly go through heat of formation of some of the substances in this slide. We have fuels and let us consider hydrocarbons. A hydrocarbon could be saturated, it could be unsaturated, it could be aliphatic, it could be aromatic. What do we mean by all this, that you would have studied in your high school chemistry? All what we mean is if the carbon atom in the hydrocarbon are fully saturated that means the C C and CH all are single bonds. We say the hydrocarbon is an aliphatic substance. If you say aromatic well you have something like a change a benzene ring of 6 carbon atoms with alternate double bonds.

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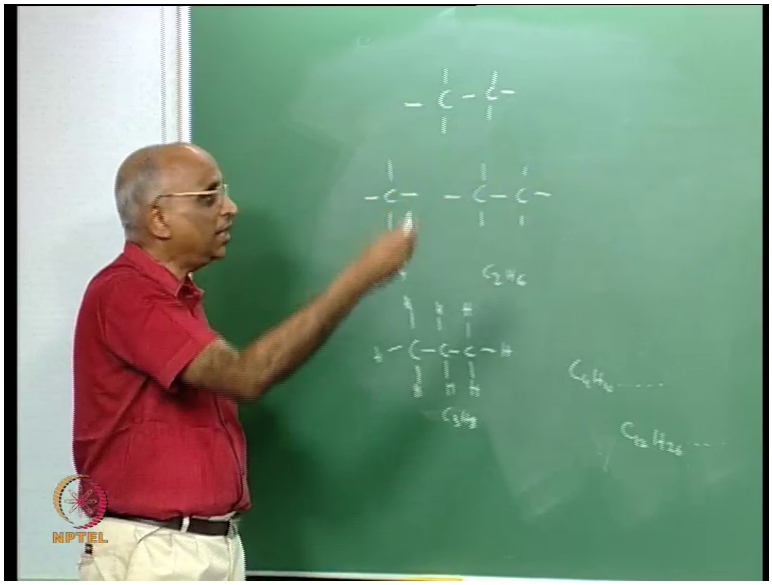

Substances, which have this benzene ring structure are known as aromatic substances. Getting back to saturated hydrocarbons. The simplest hydrocarbon is methane, the next one is ethane that is CH_4, C_2H_6. The next is propane C_3H_8 and then butane C_4H_{10} and so on. The chain keeps increasing and we come to kerosene - it is little longer chain Do-decane $C_{12}H_{26}$ and further up we have lubricating oils and so on.

If we determine the heat of formation of let us say methane; it is −74.9 kJ/mole, ethane is −84.7 kJ/mole. Propane, which is C_3H_8, is −103.9 kJ/mole while butane is −124.7 kJ/mole. Kerosene has a value of −293 kJ/mole. This means a fuel as it becomes more and more complicated in structure or more and more longer in chain has a higher negative value of heat of formation. If we go to a polymer and what is a polymer? It consists of chains of carbon and hydrogen and perhaps oxygen and nitrogen and its heat of formation is something like −60 kJ/mole. But the polymer does not come in this particular family of the saturated hydrocarbons. It consists of unsaturated double bonds and we will be dealing with it when we study solid propellants.

Let us summarize the trends in the values of heat of formation of fuels. For simple substances with minimum saturated bonds, the heat of formation has a small but negative value. The value of heat of formation becomes more negative as the substance becomes more and more complex with a large number of bonds. That means that we can write it as large negative values; this is just based on methane ethane propane and all that up to kerosene.

If you take a substance like hydrogen, which is an element, the standard heat of formation is 0. There are certain substances, which are known as explosives. Explosives are substances that have in built oxygen in them. This means that explosives contain both fuel and oxygen within it as compared to a fuel that reacts with an extraneous oxidizer to form products of combustion.

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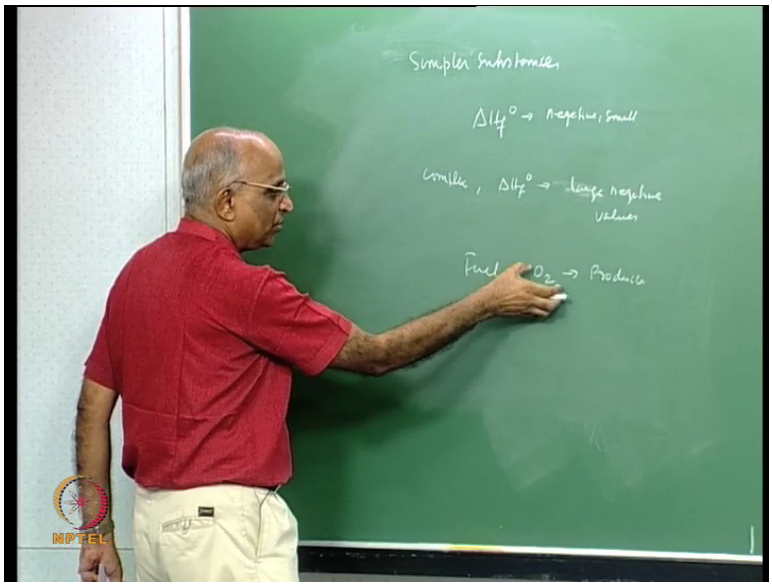

Hydrogen peroxide H_2O_2 can be considered as an explosive since it dissociates to form water and hydrogen. It has inbuilt fuel hydrogen and oxygen. Similarly, you have substances containing nitrogen such as hydrazine N_2H_4 and this is an explosive because by itself it could react to form products.

The explosive hydrogen peroxide has a heat of formation of −187.8 kJ/mole while hydrazine N_2H_4 has a small but positive value of heat of formation. It is + 50 kJ/mole. And what are the values of heats of formation if we were to consider some other explosive like nitroglycerin. What is nitro glycerine? Nitroglycerine is glycerine known as propane triol and the propane triol has chemical formula $C_3H_5(OH)_3$. We replace OH by NO_2 to get nitroglycerine $C_3H_5(NO_2)_3$. Its heat of formation is − 370 kJ/mole.

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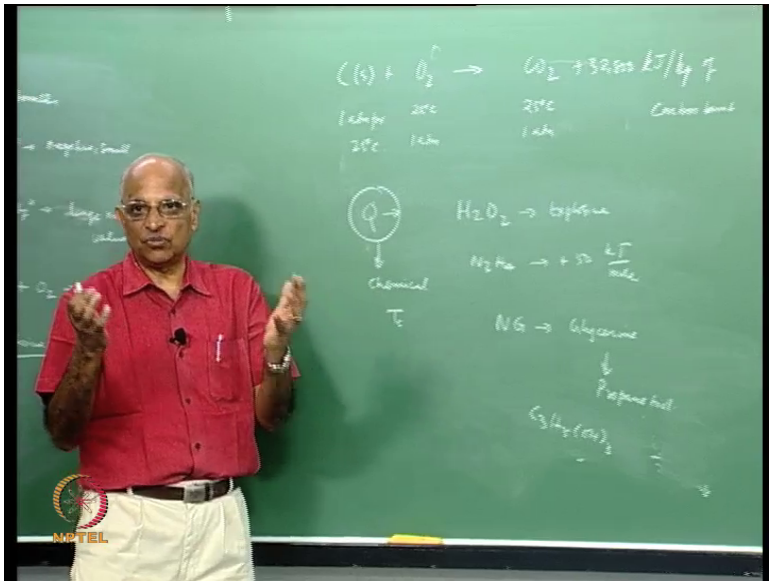

And based on the standard heats of formation of the different substances, we would like to find out which chemical when it reacts gives maximum heat. We will continue with this in the next class and we will try to find out what are the chemical substances which are most viable as propellants for rockets. We will try to zero down the number of chemicals, which can be used for rockets, to something like seven or eight.